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## NO DRAWINGS

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(54) FREE-FLOWING FUSED BEADS OF THERMOPLASTIC POLYMERS

(71) We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Midland, 5 County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to 10 be particularly described in and by the following statement: —

This invention relates to the preparation of free-flowing fused thermoplastic beads.

Dry, free-flowing powders of thermo- 15 plastic polymers are used extensively in the production of thin sheets, films, coatings and especially rotationally molded articles.

Powders currently used for such purposes are often prepared by melting low density 20 polymer particles to fuse the polymer into a single mass that is substantially free of dissolved gas and then grinding the mass into a fine powder. This process is expensive and usually produces rough, irregular 25 particles which are not free-flowing. In addition, the resulting powders have low bulk densities and are not ideally suited for the above purposes.

Known methods for preparing free- 30 flowing powders of organic polymer require that the polymer be dissolved in an inert, organic solvent and then precipitated by the removal of the solvent. In many instances the presence of solvents during the 35 preparation of free-flowing powders is undesirable, primarily because their removal is difficult and time consuming.

Since the use of solvent in conventional methods is the cause of many problems and 40 considerable expense, it would be highly desirable to provide an inexpensive method which does not require dissolving the polymer in a solvent in order to prepare dry free-flowing powders of thermoplastic 45 organic polymers.

In accordance with the present invention, free-flowing fused beads of normally solid, thermoplastic organic polymers are prepared by a method comprising the steps of (1) suspending a fine powder of a normally solid, water-insoluble, thermoplastic organic polymer in an aqueous medium containing from 0.05 to 20 weight percent based on the polymer of a suspending agent which is essentially non-reactive with and insoluble in the medium and the polymer, (2) heating the resulting suspension to a temperature being at least at the melting point of the polymer while subjecting the suspension to agitation and 50 (3) cooling the suspension while continuing the agitation until the molten polymer solidifies to form substantially spheroidal, free-flowing fused beads having greater size, usually from 2 to 100 times, than the 55 powder particles from which they were made. In addition, such beads usually have a bulk density ranging from about one half to three times that of the starting powder.

Beads produced in the practice of this invention are useful in static or fluidized dip coating, spraying, dusting and flame spraying applications. They can also be used in the preparation of molded or 70 formed shapes particularly by means of a rotational molding process. In addition, such beads eliminate the need for expensive specialized extruders needed to accept the 75 powders produced in some polymerization processes.

The process of this invention requires, as starting materials, finely divided particles of a normally solid, water-insoluble, thermoplastic organic polymer; an aqueous suspending medium; and an essentially non-reactive, insoluble suspending agent.

Free-flowing fused beads of any thermoplastic water-insoluble organic polymer may be prepared by this invention. Examples include the polymers of  $\alpha$ -olefins and halo- 90

substituted  $\alpha$ -olefins such as ethylene, propylene, 1-butene, 1-hexene, or vinyl chloride; polymers of monovinyldene aromatic compounds such as styrene,  $\alpha$ -methylstyrene,  $\alpha$ -methylstyrene, or  $\alpha$ -butylstyrene; polymers of the alkyl acrylates and derivatives thereof, such as ethyl acrylate, methyl methacrylate,  $n$ -butyl acrylate, or acrylonitrile; polymers of other ethylenically unsaturated monomers such as vinyl acetate; and copolymers of above-listed monomers such as ethylene and butene-1, ethylene and ethyl acrylate, styrene and butyl acrylate, ethyl acrylate and 15 methyl methacrylate, or  $\alpha$ -methyl styrene and 2-ethylhexyl acrylate. Methods for the preparation of these polymers and copolymers are described fully in Schildknecht, Polymer Processes, Vol. X (1956).

20 Aqueous media suited for the purposes of this invention include water and aqueous solutions of various surfactants and wetting agents. The presence of surfactant in the aqueous medium is optional; however, the use of surfactant is often desirable as a means of controlling particle size. When used, the surfactant is usually present in small amounts ranging from 0.001 to 1.0 weight percent based on the polymer. Preferred amounts of surfactant vary with the particle size desired, the particular surfactant used, type of suspending agent and polymer type. Generally, an increase in the amount of surfactant results in the formation of smaller beads. Surfactants which may be used are the known water-soluble surface active agents, particularly the anionic-type, for example the sulfated and sulfonated compounds, and soaps of monocarboxylic acids. 35 Specifically, the sulfated and sulfonated compounds include sodium dodecyl benzene sulfonate, sodium oleyl sulfate, ammonium dodecyl sulfonate, potassium lauryl sulfate, and the alkali salts of sulfonated polystyrene. 40 Specific examples of soaps of monocarboxylic acids include sodium laurate, calcium stearate, and potassium palmitate. Non-ionic surfactants which may be utilized include the polyoxyethylene ethers of the 45 higher fatty alcohols, the alkyl phenols and others set forth in Becher, Emulsions: Theory and Practice, 2nd ed., Reinhold Publishing Corporations, New York, 221-225 (1965). Ampholytic surfactants such as 50 disodium-N-tallow- $\beta$ -iminodipropionate and cationic surfactants such as octadecylammonium chloride and others described in Becher, supra, on page 221 are also suitable.

55 Suspending agents preferred for use in this invention are inorganic compounds in the form of water-insoluble powders or precipitates which are also insoluble in and substantially non-reactive with the thermoplastic organic polymer. Preferred examples 60 which are insoluble in suitable aqueous media include kaolin, barium sulfate, zinc oxide, talcum, aluminum hydroxide, tricalcium phosphate, neutral calcium oxalate, titanium dioxide, insoluble and slightly 65 neutral phosphates, hydrated complex magnesium silicates, and colloidal clays. Other agents such as the natural polymeric agents, modified natural polymeric agents such as methyl cellulose, synthetic polymeric agents, low molecular compounds, and combination agents listed on pp 78-81 of Schildknecht, Polymer Processes, Vol. X, (1956), are operable, but the above-listed 70 inorganic agents are preferred. Suspending 75 agents are used in amounts ranging from 0.05 weight percent to 20 weight percent based on the polymer, with preferred amounts varying with the particular agent used and desired size. As an illustration, a 80 level of 10 weight percent of zinc oxide and 50 ppm disodium-N-tallow- $\beta$ -iminodipropionate are used when particles of 100-400 millimeters are desired, whereas 4 weight percent of tricalcium phosphate and 50 ppm 85 of the same surfactant are sufficient for producing the same size particle.

85 For the purposes of this invention, the ratio of suspending medium to polymer powder is such that a stirrable slurry 90 results. Good results, i.e., particles having a more uniform size and rounded shape, are obtained with medium-to-powder ratios ranging from 1:2 to 30:1 by weight, with the best results obtained in suspensions 95 having medium-to-powder ratios from 5:1 to 10:1.

95 The polymer powder is dispersed in the suspending medium, i.e. an aqueous liquid containing 0.05 to 20 percent of a 100 suitable suspending agent, with any conventional mixing apparatus, for example, a baffled tank equipped with stirrer means.

100 The suspension is heated to a temperature at or above the crystalline melting 105 point of the polymer, but low enough to avoid degradation of the polymer. It is necessary to maintain the suspension at these temperatures for a period sufficient to permit the initial particles to become 110 molten. In preferred embodiments the suspension is maintained above the melting point for 5 minutes or more. It is generally desirable to conduct the heating step in a 115 closed vessel and at pressures sufficient to 120 maintain the suspending medium in the liquid state. Pressures from 20 to 200 pound per square inch (1.4-14.5 atmospheres) are generally sufficient to accomplish this end.

125 Throughout the heating step the suspension is agitated at a rate such that the molten particles are not permitted to coagulate into a single mass. The desired rate for a particular system can be readily determined by the skilled artisan. As an illus- 130

tration of the invention, the rates of agitation suitable for small reaction vessels equipped with loop stirrers and having a total volume from 5 to 10 liters range from

5 200 to 1400 rpm. In preferred embodiments, the agitation has an up-and-down motion in addition to centrifugal motion which keeps the molten polymer dispersed through out the suspending medium. This desired 10 up-and-down portion can be accomplished with pitched blade stirrers; however, adequate up-and-down motion can also be achieved with loop stirrers. As a general rule, the particular rate of agitation affects 15 particle size to some extent, but has less influence than the suspending agent and surfactant so long as it is sufficient to prevent coagulation into a single mass.

The initially formed molten droplets of 20 polymer agglomerate and coalesce to form larger spheroidal droplets. As these droplets reach the desired size, the suspension is cooled while continuing the same rate of agitation used in the heating step. The 25 method of cooling and rate of cooling are not critical in the practice of invention so long as the specified agitation rate is maintained until molten droplets solidify.

The resulting beads are separated from 30 suspending medium and then washed to remove suspending agent. In one embodiment, 0.1 N HCl is used to remove zinc oxide and tricalcium phosphate, followed by a water rinse to remove the acid.

35 In most embodiments, the resulting beads are fused solid spheroids having virtually no porosity and average diameters substantially greater than that of the starting particles, in some instances, up to about 5 40 millimeters. However, under certain conditions, the resulting beads are actually agglomerates of smaller particles, said agglomerates having void spaces therein. In such instances, the beads are free-flowing 45 and have increased size, but do not have substantially increased bulk densities.

The following examples illustrate the

invention. All parts and percentages in the specification and claims are weight percentages unless otherwise indicated.

50

*Example 1*

A 300-gram portion of linear polyethylene (Melt Index = 12, molded density = 0.953) having an average particle diameter 55 of less than .075 mm and bulk density of 16 pounds per cubic foot (256 g./l.) was charged to a 6-liter agitated, baffled, steel reactor, 7 inches (17.5 cm.) in diameter and 10 inches (25 cm.) deep with four 1/2 inch 60 (1.27 cm.) baffles on the walls thereof. The reactor was equipped with a pitched blade stirrer and contains 3 liters of water, 30 grams of ZnO and 0.015 grams of disodium-N-tallow- $\beta$ -iminodipropionate. The resulting 65 mixture was agitated at 1200 rpm and heated with stirring to 140°C. at which point the pressure of the reactor is 50 to 60 psi (4.4-5.1 atmospheres). These conditions were held for 2 hours after which the mixture was cooled. The resulting particles, after separating from the medium by centrifuging, washing with 0.1 N HCl, rinsing with water, and drying, were found to be free-flowing fused beads having a bulk 70 density of 26.5 lbs/ft<sup>3</sup> (242 g./l.) and an average bead diameter of 0.250 to 0.840 mm.

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*Examples 2-7*

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Numerous samples of beads were prepared by following the procedure of Example 1 except that an ethylene/butene-1 copolymer powder was dispersed in an aqueous medium having varied amounts 85 and types of suspending agents and then heated at maximum temperature for different periods of time. The bead size and bulk density of each sample are shown in Table 1. For the purposes of comparison 90 and to particularly point out the advantages of this invention, the bulk density and particle size of the starting raw powder, designated C, are also listed in Table 1.

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TABLE I

Example No.	Water ml.	Polymer Powder g.	Suspending Agent	Surfactant g.	Temp. °C	Time held at max. temp. hr.	Bulk density lb./cu.ft.	Bead Size, mm. (1)
C*	3000	150	ZnO	3.0	0.015	140	1.5	256 90% in 0.125
2	3000	300	ZnO	3.0	0.015	140	2.5	560 87% in 0.150
3	3000	300	ZnO	1.0	0.015	134	0.1	512 86% in 0.050-0.420
4	3000	300	TiO <sub>2</sub>	3.0	0.015	140	1.5	288 96% in 0.250-0.841
5	3000	300	TiO <sub>2</sub>	1.0	0.015	134	1.5	512 88% in 0.125-0.420
6	3000	300	TiO <sub>2</sub>	7	3000	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	6	0.015 134 0.1 31 496 96% in 0.50-1.41

\* Not an example of the invention  
(1) Bead is the average diameter of the beads as determined by screen analysis where the proportion of beads passing through a screen of predetermined mesh size is measured. Screens having mesh sizes of 0.044, 0.074, 0.125, 0.149, 0.250, 0.420, 0.500, 0.841, 1.410, 2.000 and 4.000 millimeters were used.

thermoplastic polymer in an aqueous medium in proportions such that a stirrable slurry results, the aqueous medium containing from 0.05 to 20 weight percent based on the polymer of a solid suspending agent, said agent being insoluble in and substantially non-reactive with the polymer and the medium; (2) heating the resulting suspension to a temperature at least equal to the melting point of the polymer while agitating the suspension; and (3) cooling the suspension while continuing the agitation until the molten polymer solidifies to form beads having greater size than the particles of the powder.

2. A method according to Claim 1 wherein the polymer is a linear polyethylene.

3. A method according to Claim 1 wherein the polymer is an ethylene/butene-1 copolymer.

4. A method according to Claim 1 wherein the polymer is polypropylene.

5. A method according to Claim 1 wherein the polymer is polystyrene.

6. A method according to any one of the preceding claims wherein the suspending agent is an inorganic suspending agent in the form of a powder.

7. A method according to any one of the preceding claims wherein the suspending agent is zinc oxide, titanium dioxide or calcium phosphate.

8. A method according to any one of the preceding claims wherein a surfactant is used in addition to the suspending agent.

9. A method according to claim 8 wherein the surfactant is present in an amount ranging from 0.001 to 1.0 percent by weight of the polymer.

10. A method according to Claim 8 or 9, wherein the surfactant is disodium-N-tallow-β-iminodipropionate.

11. A method according to any one of the preceding claims wherein the resulting suspension is heated for a period of at least 5 minutes.

12. A method for preparing free-flowing fused beads of a normally solid, water-insoluble, thermoplastic organic polymer substantially as described hereinbefore with reference to any one of the specific examples.

13. Free-flowing fused beads of a normally solid, water-insoluble, thermoplastic organic polymer whenever produced by the method defined in any one of the preceding claims.

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WHAT WE CLAIM IS:—  
1. A method for preparing free-flowing fused beads of a normally solid, water-insoluble, thermoplastic, organic polymer, comprising (1) suspending a powder of the

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